

University of Groningen

## Photon Echoes in the $3P_0 \leftarrow 3H_4$ Transition of $\text{Pr}^{3+}/\text{LaF}_3$

Morsink, Jos B.W.; Wiersma, Douwe A.

*Published in:*  
Chemical Physics Letters

*DOI:*  
[10.1016/0009-2614\(79\)80137-2](https://doi.org/10.1016/0009-2614(79)80137-2)

**IMPORTANT NOTE:** You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1979

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Morsink, J. B. W., & Wiersma, D. A. (1979). Photon Echoes in the  $3P_0 \leftarrow 3H_4$  Transition of  $\text{Pr}^{3+}/\text{LaF}_3$ . *Chemical Physics Letters*, 65(1). [https://doi.org/10.1016/0009-2614\(79\)80137-2](https://doi.org/10.1016/0009-2614(79)80137-2)

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

**PHOTON ECHOES IN THE  $^3P_0 \leftarrow ^3H_4$  TRANSITION OF  $\text{Pr}^{3+}/\text{LaF}_3$** 

Jos B.W. MORSINK and Douwe A. WIERSMA

*Department of Physical Chemistry, 9747 AG Groningen, The Netherlands*

Received 21 April 1979

Photon-echo quantum beats observed in the two-pulse and three-pulse photon echo of the  $^3P_0 \leftarrow ^3H_4$  transition in  $\text{Pr}^{3+}/\text{LaF}_3$  were used to determine the excited-state spin-hamiltonian. In addition we report on the anomalous stimulated photon echo observed in the same transition which in a magnetic field may acquire a lifetime of about 30 minutes.

In recent years a number of coherent optical studies have been performed on the  $^3P_0 \leftarrow ^3H_4$  and  $^1D_2 \leftarrow ^3H_4$  optical transition of  $\text{Pr}^{3+}$  in  $\text{LaF}_3$ . In particular the  $^1D_2 \leftarrow ^3H_4$  transition was studied in detail using the techniques of fluorescence line-narrowing [1], optical free-induction decay [2,3], saturation absorption spectroscopy [4] and photon echo [5]. Also optical-rf double-resonance measurements on the ground state were carried out [6] which led to the evaluation of hyperfine splittings in the ground electronic state. The  $^3P_0 \leftarrow ^3H_4$  transition, which is presently not easily accessible using cw dye-laser excitation, has only been studied with the photon-echo technique.

Takeuchi and Szabo [7] were the first to report photon echoes in this transition while Takeuchi [8] presented the first measurement of the dephasing time of this transition. Quite recently Yamagishi and Szabo [9] studied the concentration dependence of the photon-echo decay and concluded that, up to 1.0%  $\text{Pr}^{3+}$ , the echo decay was unaffected.

Chen and Hartmann [10] and Chen et al. [5] however showed that the photon-echo decay in  $^3P_0 \leftarrow ^3H_4$  is modulated and that therefore the initial echo decay time as reported by Yamagishi and Szabo is not a meaningful parameter. This point of view is supported by recent coherent transient studies on the  $\text{Pr}^{3+}/\text{LaF}_3$  system by Shelby et al. [11] from which an echo lifetime of 20  $\mu\text{s}$  was suggested. We note here that all photon-echo measurements referred to were performed using an optical delay line, which makes such measurements not only cumbersome but also not dependable

enough for detailed analysis.

We have recently shown [12] that photon-echo measurements could be done much more easily and dependably using two nitrogen-pumped dye-lasers. In this letter we show that in the case of a photon-echo study of a multilevel system, like the  $^3P_0 \leftarrow ^3H_4$  transition, such a set-up is essential.

The main reason for picking the  $^3P_0 \leftarrow ^3H_4$  transition of  $\text{Pr}^{3+}/\text{LaF}_3$  for a photon-echo study, however, is our recent finding [13,14] of a new type of stimulated photon echo in systems where optical branching occurs.

The lifetime of this optical echo is only dependent on the lifetime of the levels in the electronic ground state and the prediction was that in "simple" level systems the echo lifetime could be very long. From the work of Chen et al. [5] we concluded that in the  $^3P_0 \leftarrow ^3H_4$  transition, optical branching occurs and from Erickson's work [6] we know that the lifetime of the hyperfine levels in the ground state at 4.2 K is  $\approx 0.5$  s. This optical transition therefore seemed ideal for our purpose to seek confirmation of the proposed anomalous stimulated echo formation mechanism.

In the course of measurements on the anomalous photon echo we also were set-up to measure easily the two-pulse and regular stimulated photon echo. The results of these measurements contained so much more detail than has been published [5] that it seems worthwhile to report them here.

In the experiments presented we used a crystal with  $\approx 1$  atom per cent  $\text{Pr}^{3+}$  in  $\text{LaF}_3$ . The experimental

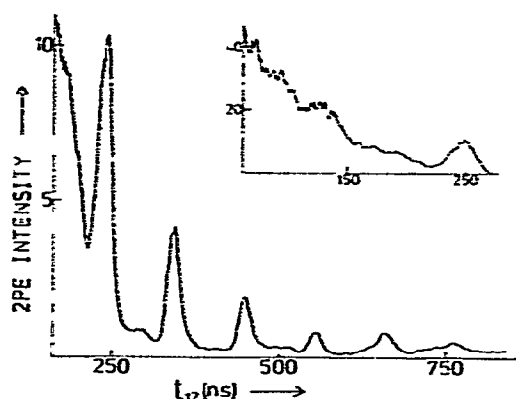


Fig. 1. Two-pulse photon-echo intensity versus excitation pulse delay in the  $^3P_0 - ^3H_4$  transition of  $\text{Pr}^{3+}$  in  $\text{LaF}_3$  at 2 K.

set-up was identical to that described previously [12].

In fig. 1 the regular two-pulse photon-echo (2PE) decay is shown using two dye-lasers. The total time required for taking such a continuous trace is only 5 min. which clearly shows the advantage of this set-up over the one using an optical delay-line. Particularly noteworthy is the beat pattern, which corresponds to the 8.47 MHz splitting between the  $|\pm 1/2\rangle$  and  $|\pm 3/2\rangle$  hyperfine levels in the electronic ground state. The initial echo decay (up to 200 ns) time is identical to the one reported in ref. [9]. The relative intensity of the beats indicates that the excited-state levels are heavily mixed in terms of the ground-state basis set. We further note that the "sharpness" of the quantum beats indicates that the observed modulation cannot be due to a single frequency, but that interference between at least two frequencies, which are multiples of one another, must occur.

Fig. 2 shows that the stimulated photon echo (3PSE) also exhibits strong modulations, albeit on a time scale, where the 2PE is not detectable. As in the electronic ground state the hyperfine splittings far exceed the modulation frequencies observed in the 3PSE decay, we conclude that the observed modulation frequencies are due to quadrupole splittings in the excited state. Note that the background signal on which the beats occur is appreciable compared to the one observed in the 2PE decay. We further remark that, as shown by Mims [15], in the 3PSE decay the intensity of modulation is strongly influenced by the

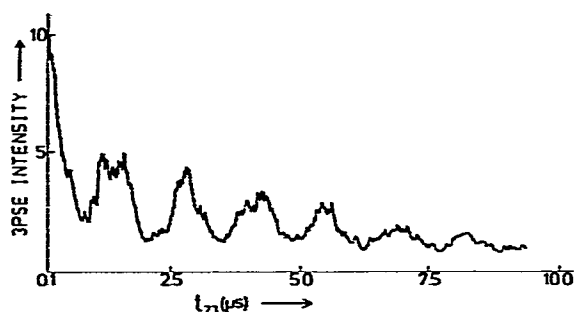


Fig. 2. Stimulated photon-echo intensity versus second-third excitation pulse delay at 2 K in the  $^3P_0 - ^3H_4$  transition of  $\text{Pr}^{3+}$  in  $\text{LaF}_3$ . The separation between the first two excitation pulses is 50 ns.

separation between the first two excitation pulses. In an attempt to understand the basic echo modulation patterns and to determine the excited state ( $^3P_0$ ) spin-hamiltonian we have calculated photon-echo beat patterns with different choices of the excited-state spin parameters. Erickson [6] has shown that the  $^3H_4$  electronic ground state may be very well described by the following pseudo-quadrupole spin-hamiltonian of the  $\text{Pr}^{3+}$  nucleus ( $I = 5/2$ ):

$$H = P[I_z^2 - \frac{1}{3}I(I+1)] + \frac{1}{6}\eta(I_+^2 + I_-^2) \quad (1)$$

where  $P = 4.185 \pm 0.003$  MHz and  $\eta = 0.105 \pm 0.010$ . This hamiltonian leads to Kramers-degenerate nuclear spin levels where the splitting between the  $|m_I| = 5/2$  and  $3/2$  levels is twice the splitting between  $|m_I| = 3/2$  and  $1/2$  levels. This is consistent with the 2PE decay as noted. Consideration of the total spin-hamiltonian shows that the calculated spin-splittings are predominantly due to second-order hyperfine coupling effects [5]. The effect of the quadrupole in the description of the ground state therefore can effectively be taken care of as part of the hyperfine coupling term.

In the excited  $^3P_0$  state however the situation is drastically different [5]. Second-order hyperfine coupling is expected to be negligible and the only interaction that lifts the  $|m_I|$  degeneracy is the quadrupole-electric-field-gradient interaction. As only one of the principal axes of the quadrupole tensor needs to be collinear with one of the principal axes of the hyperfine tensor [5] one may not expect that the ground

and excited hamiltonians commute. This means that optical branching occurs and the precise orientation of the two principal-axes systems determines the branching ratios. Presently no information is available on the relative orientation of these axes systems; therefore we have taken a poor man's approach and performed calculations on the system using an analogous spin-hamiltonian as defined in eq. (1) with varying  $\eta$  values. The relation between this pseudo-hamiltonian and the real one in the excited state can only be determined when information on the relative orientation of the different principal-axes systems becomes available.

Using the expression in eq. (5) of the paper by Lambert et al. on echo modulation [16] we have calculated for several  $\eta$  values the 2PE modulation spectrum. Essential in this calculation was that the echo intensity was taken as the sum of the squared polarizations of three four-level systems. For the 2PE modulation-calculation the four-level system consists of three ground-state levels,  $-1/2$ ,  $3/2$ ,  $-5/2$  and one excited-state level (e.g.  $|-1/2'\rangle = c_1|-1/2\rangle + c_2|3/2\rangle + c_3|-5/2\rangle$ ). It turns out that for  $\eta \approx 3$ , we find good agreement between the calculated and observed 2PE modulation spectrum. With this choice of  $\eta$  the 3PSE modulation spectrum can also be explained if for  $P$  we take 0.096 MHz. We note here that from the spin hamiltonian (1) with the parameters just mentioned, in the excited  $^3P_0$  state the splitting between the  $|m'_I| = 3/2$  and  $1/2$  levels is twice the splitting between the  $|m'_I| = 5/2$  and  $3/2$  levels. The levels defined in terms of the  $m_I$  quantum number are thus heavily mixed by the  $\alpha$ -symmetry term in eq. (1). We also note that the chosen spin-hamiltonian explains the sharp recurrences in the 2PE decay and that indeed the sharpness is a consequence of an interference effect between the three ground-state frequencies. The parameters of our spin-hamiltonian are substantially different from the ones estimated by Chen et al. [5]. The 3PSE modulations however clearly exhibit the excited-state splittings. It is also interesting to note that, in complete agreement with expectation, the spin splittings in the states increase in the order  $^3P_0 < ^1D_2 < ^3H_4$ .

To conclude this discussion on photon-echo modulation we remark that the success of the analysis is partly due to the fact that the ground- and excited-state spin splittings are so widely different that the

modulation frequencies occur on different time scales.

We now turn to a discussion of the stimulated photon echo that inspired this work. As expected the 3PSE in this transition has a component with a very long lifetime ( $\approx 0.5$  s!) which far exceeds the fluorescence lifetime ( $\approx 47$   $\mu$ s). In a previous letter [14] we explained this anomalous photon echo as resulting from optically induced nuclear spin polarization.

Briefly, the first two excitation pulses create a frequency grating at the optical transition frequency and simultaneously induce a *frequency dependent* nuclear spin polarization in the electronic ground state. The important point to note is that there exists for every site a one-to-one correspondence between the optical and nuclear spin polarization. When a third probe pulse comes along, at a time that the optical polarization is lost, it re-excites from the nuclear spin polarization a frequency grating which mimics the situation at the time of the second pulse. This of course leads to the formation of an optical echo. For further details see refs. [14,17].

We have also observed that the lifetime of the anomalous photon echo is strongly dependent of the magnetic field. In fig. 3 we show a picture of the anomalous echo intensity at 2 K in a magnetic field of 4.8 T perpendicular to the crystal  $c$ -axis. The upper

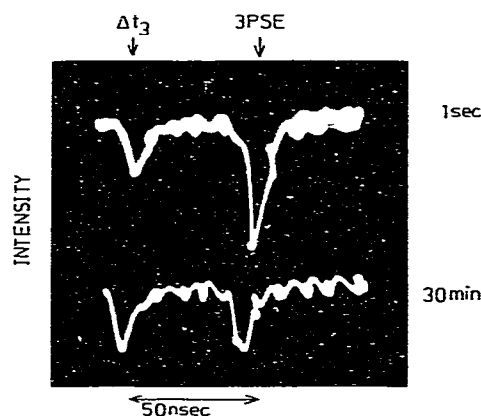


Fig. 3. Anomalous stimulated photon-echo trace observed after the third probe pulse in a magnetic field of 4.8 T at 2 K (the first pulse on the left is the probe pulse). The upper trace was obtained at 1 s after the second pulse. The lower trace was taken at 30 minutes after the second pulse. The first two excitation pulses were separated by 50 ns.

trace was taken with the third pulse following the second pulse after 1 s, while the lower trace was obtained at 30 minutes after the second pulse. From the modulations observed in the 3PSE intensity versus magnetic field we conclude that at this high field optical branching still occurs, which implies a small nuclear g-factor for this magnetic field orientation. We tentatively interpret the effect of the magnetic field on the nuclear spin relaxation in terms of suppression of fluorine and/or lanthanum spin cross relaxation processes. This point needs further investigation.

In summary, we have shown that from the photon-echo quantum beats in the 2PE and 3PSE, the excited-state spin-hamiltonian may be determined. Furthermore we have shown that stimulated photon echoes with an extremely long lifetime may be generated which are a consequence of optical branching. The interesting feature of this echo is that its lifetime solely depends on the hyperfine levels of the electronic ground state.

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

## References

- [1] L.E. Erickson, Opt. Commun. 15 (1975) 246.
- [2] A.Z. Genack, R.M. Macfarlane and R.G. Brewer, Phys. Rev. Letters 37 (1976) 1078.
- [3] R.M. Shelby and R.M. Macfarlane, Opt. Commun. 27 (1978) 399.
- [4] L.E. Erickson, Phys. Rev. B16 (1977) 4731.
- [5] Y.C. Chen, K.P. Chiang and S.R. Hartmann, Opt. Commun. 26 (1978) 269.
- [6] L.E. Erickson, Opt. Commun. 21 (1977) 147.
- [7] N. Takeuchi and A. Szabo, Phys. Letters 50A (1974) 361.
- [8] N. Takeuchi, J. Luminescence 12/13 (1976) 743.
- [9] A. Yamagishi and A. Szabo, Opt. Letters 2 (1978) 160.
- [10] Y.C. Chen and S.R. Hartmann, Phys. Letters 58A (1976) 201.
- [11] R.M. Shelby, C.S. Yannoni and R.M. Macfarlane, Phys. Rev. Letters 41 (1978) 1739.
- [12] J.B.W. Morsink, T.J. Aartsma and D.A. Wiersma, Chem. Phys. Letters 49 (1977) 34.
- [13] W.H. Hesselink and D.A. Wiersma, Chem. Phys. Letters 50 (1977) 51.
- [14] J.B.W. Morsink, W.H. Hesselink and D.A. Wiersma, Chem. Phys. Letters 64 (1979) 1.
- [15] W.B. Mims, in: Electron paramagnetic resonance, ed. S. Geschwind (Plenum Press, New York, 1972) ch. 4.
- [16] L.Q. Lambert, A. Compagnon and I.D. Abella, Phys. Rev. A4 (1977) 2022.
- [17] J.B.W. Morsink and D.A. Wiersma, to be published.